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B32B 5/18**(21)Application number : **05-285247**(71)Applicant : **SUMITOMO OSAKA CEMENT
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YAMAZAKI YUSUKE****(54) POROSITY-GRADIENT TYPE LIGHTWEIGHT CERAMIC COMPACT AND ITS PRODUCTION****(57)Abstract:**

PURPOSE: To provide a porosity-gradient type lightweight ceramic compact, having high strength and surface smoothness and capable of manifesting excellent thermal shock resistance.

CONSTITUTION: This porosity-gradient type lightweight ceramic compact is composed of oxide-based or nonoxide-based ceramics and has the following properties: (a) the porosity of the whole compact is 30-90%; (b) a dense layer is present over a depth of 5-55 μ m from the surface and (c) the porosity continuously increases from the dense layer to the central part of the compact. This method for producing the ceramic compact is to add a foaming liquid having 10-2000 μ m cell diameter to a slip of oxide- or nonoxide-based ceramic powder, stir the resultant mixture, carry out the slip casting of the obtained slip at 110 μ m/min casting rate, then demold the formed compact, degrease the demolded compact and bake the degreased compact.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]

[Industrial Application] This invention begins the setter who uses at the time of baking of an electronic material, a ceramic material, the charge of a powder alloy, etc., a sagger, etc., and relates to the porosity dip mold lightweight ceramic Plastic solid which can be broadly used in various industrial fields, and its manufacture method.

[0002]

[Description of the Prior Art] As a result of heat capacity's also becoming small since the specific gravity is small when using this as baking tool material, the conventional lightweight ceramic Plastic solid which consists of a porous body has little heat energy which heating of burning tools takes, and ends. Therefore, as compared with the case where the usual ceramic Plastic solid is used, good thermal efficiency is acquired and there is an advantage that a manufacturing cost can be held down.

[0003] However, a porous body, therefore reinforcement are low, and since pore is moreover exposed to a surface, there is a problem that a small calcinated object falls to exposure pore, and baking becomes imperfection.

[0004] And although there is a defect that generally a lightweight ceramic Plastic solid is inferior to thermal shock resistance, this originates in existence of pore. That is, in the lightweight ceramic Plastic solid which consists of a porous body, as long as pore existed, there was a limit also in an improvement of thermal shock resistance naturally.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, this invention sets it as the main objects to offer the porosity dip mold lightweight ceramic Plastic solid which can demonstrate the thermal shock resistance which was excellent while having high reinforcement and surface smooth nature. Furthermore, this invention can be controlled to desired relative bulk density, and aims also at offering the manufacture method which can acquire a Plastic solid with the above-mentioned structure comparatively easily.

[0006]

[Means for Solving the Problem] this invention person came to complete a header and this invention for demonstrating a header and thermal shock resistance which was further excellent while having high reinforcement and surface smooth nature, although this Plastic solid was porosity for a Plastic solid with unique structure being acquired, when a raw material slurry which introduced foam liquid so much is fabricated by slip casting under fixed conditions, as a result of repeating research wholeheartedly in view of a problem of the above-mentioned conventional technology.

[0007] That is, this invention relates to a following Plastic solid and a following manufacture method.

[0008] 1. It is the Plastic solid which consists of an oxide system or non-oxide system ceramics, and is (a). Porosity of the whole Plastic solid is 30 - 90%, and it is (b). A substantia-compacta layer exists covering a depth of 5-50 micrometers from a front face, and it is (c). Porosity dip mold lightweight ceramic Plastic solid characterized by porosity increasing from the substantia-

compacta layer concerned continuously toward a Plastic solid core.
[0009] 2. Manufacture method of porosity dip mold lightweight ceramic Plastic solid characterized by unmolding, degreasing and calcinating after diameter of air bubbles carries out slip casting of slurry which adds and comes to agitate foam liquid which is 10-2000 micrometers to oxide system or non-oxide system ceramic powder slurry below by casting rate/of 110 micrometers.

[0010] Hereafter, it explains per Plastic solid of this invention.

[0011] a Plastic solid with which a porosity dip mold lightweight ceramic Plastic solid of this invention consists of an oxide system or non-oxide system ceramics -- it is -- the surface Porosity of the whole (a) Plastic solid is 30 - 90%. (b) substantia-compacta layer -- a depth of a front face to 5-50 micrometers -- crossing -- alike -- existing -- and -- It has unique structure where (c) porosity increases from the substantia-compacta layer concerned continuously toward a Plastic solid core.

[0012] If applicable to a manufacture method shown in a postscript as construction material of a Plastic solid, what kind of ceramics is sufficient and all ceramics can adopt substantially a well-known oxide system or a well-known non-oxide system as construction material of a Plastic solid of this invention. Specifically, an alumina system, a mullite system, a zirconia system, etc. are one of things of an oxide system. Moreover, as a thing of a non-oxide system, a silicon carbide system, a silicon nitride system, an aluminum nitride system, a boron nitride system, a graphite system, etc. are mentioned.

[0013] As for especially porosity of the whole Plastic solid, it is usually desirable that it is 50 - 80% about 30 to 90%. It stops being able to demonstrate a property as a lightweight object and is not desirable when the above-mentioned porosity is less than 30%. If it exceeds 90%, reinforcement will fall. In addition, although magnitude of pore is based also on construction material which constitutes a Plastic solid, it is usually about 20-4000 micrometers.

[0014] A substantia-compacta layer usually exists covering a depth of 5-50 micrometers from a front face of a Plastic solid. A substantia-compacta layer as used in the field of [here] this invention means a layer whose porosity is usually about 0 - 5%. When [both] this substantia-compacta layer is less than 5 micrometers and a film from a front face, surface smooth nature and reinforcement fall. In addition, when high reinforcement is required, in a range which does not spoil lightweight nature, thickness from a front face may exceed 50 micrometers. Moreover, when thickness of a Plastic solid is thick, in a range which does not exceed one fourth of the thickness, you may exceed 50 micrometers.

[0015] In addition, smoothness (Rmax) on a front face of a Plastic solid is usually about 3-50 micrometers that what is necessary is just to set up suitably according to the amount of organic substances contained in a calcinated object, baking speed, and surface precision of a calcinated object. in addition -- since the larger one of surface roughness is advantageous also from a point which promotes degreasing when a precise field is not required -- the above -- you may become out of range and an embossing pattern may be made if needed.

[0016] A Plastic solid of this invention has structure where porosity increases from the above-mentioned substantia-compacta layer continuously toward a Plastic solid core. an increment in porosity -- it changes comparatively (dip of porosity) with manufacture conditions, raw materials to be used, and although it is not uniform, as shown, for example in after-mentioned drawing 1 or after-mentioned drawing 2 , with porosity alumina ceramics, a surface to the fixed depth is comparatively high, and it has become comparatively loose dip after that. As for porosity of a Plastic solid core, it is desirable to consider as a maximum of 95% from a strong point. In this invention Plastic solid with such unique structure, as a result of controlling progress of a crack and being able to prevent growth of a crack since porosity becomes small as it goes to a Plastic solid front face even if a crack occurs inside a Plastic solid, outstanding thermal shock resistance is discovered.

[0017] In addition, since stress concentration as a defect tends to happen the more the more it

becomes a long and slender configuration, pore in a Plastic solid has a desirable thing near a globular form as much as possible. Moreover, you may be the thing of structure of continuation pore, independent pores, or these hybrid models.

[0018] Next, a manufacture method of a Plastic solid of this invention is explained.

[0019] A ceramic slurry is prepared first. Using powder of ceramics of construction material of said Plastic solid as a raw material, water is added and a slurry is prepared according to a conventional method. As for loadings of water, it is desirable to usually consider as 20 - 50 weight section to the ceramic raw material 100 weight section. Adjustment of a slurry becomes difficult at a case of under 20 weight sections. Moreover, if 50 weight sections are exceeded, hardening after casting will take long duration. Moreover, in this invention, various additives, such as well-known lubricant and a dispersant, may be added if needed.

[0020] Next, air bubbles are introduced into a slurry by [which add and agitate foam liquid separately prepared with a foaming agent to the above-mentioned slurry] depending especially, or adding and stirring a direct frothing agent to the above-mentioned slurry.

[0021] What forms air bubbles in a ceramic slurry by adding and mixing is named a frothing agent which foam liquid said to this invention means a foamy object which consists of air bubbles prepared with a well-known foaming agent etc. here, and is said to this invention generically. That is, the above-mentioned frothing agent will not be limited especially if air bubbles can be built, but a foaming agent, a frothing agent, a surfactant, etc. are included by foaming agent of this invention. Specifically as a foaming agent, alkylbenzene sulfonates, a high-class alkylamino acid, etc. can be illustrated as surfactants, such as a protein system frothing agent and an albumen, as frothing agents, such as aluminum impalpable powder and silicon impalpable powder. In addition, it is desirable to use a protein system frothing agent in respect of a low price especially in this invention. Moreover, in this invention, a well-known thickener, a sizing agent, etc. can also be added suitably if needed. As a thickener, a sizing agent, etc., methyl cellulose, polyvinyl alcohol, saccharose, molasses, etc. are illustrated. By adding these, improvement in reinforcement of air bubbles in a slurry can be aimed at, and air bubbles can be stabilized. What is necessary is just to produce preparation of foam liquid with a conventional method using the above-mentioned foaming agent etc.

[0022] A slurry which introduced air bubbles is slushed into molds, such as a plaster mold, and a slip casting is performed according to a conventional method. In this case, although solid content which is floating on a cellular front face moves to a surface, the porosity slope characteristic of a Plastic solid can be given and controlled by casting that passing speed and considering as the following by 80-micrometer/preferably hereafter by 110-micrometer/with a casting rate in early stages of a mold. That is, when a slip casting is performed, air bubbles are first crushed by plaster mold front face, a substantia-compacta layer is formed, after that, a casting rate becomes slow gradually by formation of a substantia-compacta layer, and air bubbles come to remain. After a while, as a result of a casting rate's becoming slow further, and a path of air bubbles which remain inside a Plastic solid becoming large and the amount of air bubbles also increasing, a lightweight ceramic Plastic solid to which porosity changed from a surface toward a core is acquired.

[0023] When the above-mentioned casting rate exceeds a part for 120-micrometer/, it becomes difficult to give the slope characteristic of porosity. That is, since distribution of pore equalizes, it is not desirable. What is necessary is for there to be especially no limit and just to set it up suitably by a use of a Plastic solid etc., as long as a minimum of a casting rate can shut up air bubbles in a Plastic solid.

[0024] Moreover, if a casting rate is generally made quick, there is an inclination for a substantia-compacta layer to become thick. therefore -- for example, a thick substantia-compacta layer is the need -- occasionally -- a casting rate -- about 80-110micrometers/minute -- then, a 10-100-micrometer substantia-compacta layer can be made to usually form Furthermore, it is also possible to adjust water absorption of a plaster mold, putting in a plaster mold into a

decompression device and controlling a pressure, and to control a substantia-compacta layer in desired thickness.

[0025] It is also possible to control a degree of dip of porosity of a Plastic solid by this invention by inserting a positive electrode of a configuration of arbitration and a porous electrode of a negative electrode in a slurry which introduced air bubbles, and impressing voltage. That is, although solid content which is floating on a cellular front face moves with air bubbles toward an electrode of particle electrification and objection by impression of voltage, by changing voltage in this case, passing speed of the above-mentioned solid content can be controlled, and a dip degree can be changed. What is necessary is just to usually let voltage which should be impressed be the direct current voltage of 100-200V. Since a substantia-compacta layer will become is hard to be formed as a result of passing speed's becoming quick too much if migration of solid content is not enough and exceeds 200V, it is not desirable less than [100V]. Although it changes with a use of a Plastic solid, and classes of construction material, a control method of voltage can be performed by lowering voltage gradually, after it makes a substantia-compacta layer form and a substantia-compacta layer becomes desired thickness by impressing voltage of 200V first, for example.

[0026] Subsequently, if a conventional method is followed, it unmolds and degreases and it subsequently calcinates, this invention Plastic solid will be acquired. What is necessary is just to usually perform baking conditions at about 1300-1700 degrees C for about 1 to 5 hours.

[0027]

[Effect of the Invention] By the manufacture method of this invention, the ceramic Plastic solid which has the unique structure where porosity increases continuously especially the ceramic slurry that introduced air bubbles into the large quantity toward a Plastic solid core from the above-mentioned substantia-compacta layer since it fabricates by the slip casting, controlling a casting rate can be acquired.

[0028] It can demonstrate the outstanding thermal shock resistance while it has high reinforcement and surface smooth nature, although this invention Plastic solid is porosity. It is broadly utilizable for the use of the sagger for baking, a setter, a shelf board, heat insulating brick, etc. using the unique structure.

[0029]

[Example] An example and the example of a comparison are shown below, and the place by which it is characterized [of this invention] is made still clearer.

[0030] The lightweight ceramic Plastic solid was produced using alumina system ceramic powder as example 1 raw material.

[0031] First, 100g of water, 1.5g of polyacrylic acid ammonium salt system dispersants, and 1.5g of paraffin series wax system lubricant were added to 300g of alumina system ceramic powder, and the ceramic slurry was prepared by agitating by the propeller type mixer.

[0032] Subsequently, 300ml of foam liquid which consists of air bubbles of magnitude with an average of about 150 micrometers (20-230 micrometers of ranges) separately prepared with the protein system frothing agent which added saccharose 0.2% was added to the above-mentioned slurry, and it was agitated by the propeller type mixer. It was 0.62, when this bubble slurry was cast to the casting rate plaster mold for /of 80 micrometers, it unmolded 24 hours after and the bulk specific gravity of the acquired generation form was measured. Moreover, observation of the fracture surface of this Plastic solid checked that a 35-micrometer substantia-compacta layer was introduced into a surface, and 40-1500-micrometer pore was introduced into that interior. Moreover, pore was a globular form mostly and was the structure of the hybrid model of independent pore and continuation pore.

[0033] After heating the above-mentioned Plastic solid at 600 degrees C among air for 5 hours and degreasing, the lightweight ceramic Plastic solid of this invention was acquired by performing baking at 1500 degrees C for 2 hours. At this time, when a big camber or a big crack were not accepted in a Plastic solid and the fracture surface of a Plastic solid was observed, it

was checked that a 30-micrometer substantia-compacta layer is introduced into a surface, and 30-1200-micrometer pore is introduced into that interior. Moreover, the result investigated about the porosity from the surface of a Plastic solid to a core is shown in drawing 1 . This shows that porosity is increasing from the surface portion continuously toward a core. [0034] Furthermore, measurement about the porosity of the acquired Plastic solid, reinforcement, a spalling-proof property, etc. was also performed. The result is shown in a table 1. [0035] After casting using example of comparison 1 casting rate the plaster mold for /of 120 micrometers, it unmolded 16 hours after, and also the Plastic solid was produced like the example 1. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 1 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 1. [0036] [A table 1]

[0037] It turns out that especially this invention Plastic solid that porosity increases from the result of a table 1 in dip demonstrates the effect excellent in thermal shock resistance. [0038] an average of [which was separately prepared with the protein system frothing agent which added example 2 saccharose 0.2%] -- 200ml of foam liquid which consists of air bubbles with a magnitude of about 50 micrometers (10-120 micrometers of ranges) was added, and the Plastic solid was produced like the example 1 except having carried out 20 hours after, since stripping was cast. [0039] The investigated result is shown in drawing 1 about the porosity of the above-mentioned Plastic solid, and the porosity of a Plastic solid, reinforcement, a spalling-proof property, etc. are shown in a table 2. [0040] After casting using example of comparison 2 casting rate the plaster mold for /of 120 micrometers, it unmolded 12 hours after, and also the Plastic solid was produced like the example 1. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 2 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 2. [0041] [A table 2]

[0042] an average of [which was separately prepared with the protein system frothing agent which added example 3 saccharose 0.2%] -- 400ml of foam liquid which consists of air bubbles with a magnitude of about 200 micrometers (100-300 micrometers of ranges) was added, and the Plastic solid was produced like the example 1 except having carried out 32 hours after, since stripping was cast.

[0043] The investigated result is shown in drawing 1 about the porosity of the above-mentioned Plastic solid, and the porosity of a Plastic solid, reinforcement, a spalling-proof property, etc. are shown in a table 3.

[0044] After casting using example of comparison 3 casting rate the plaster mold for /of 120 micrometers, it unmolded 25 hours after, and also the Plastic solid was produced like the example 3. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 3 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 3.

[0045]

[A table 3]

[0046] The lightweight ceramic Plastic solid was produced using silicon nitride system ceramic powder as example 4 raw material.

[0047] First, 100g of water, 3.5g of polyacrylic acid ammonium salt system dispersants, and 1.5g of paraffin series wax system lubricant were added to 300g of silicon nitride system ceramic powder, and the ceramic slurry was prepared by agitating by the propeller type mixer.

[0048] Subsequently, 300ml of foam liquid which consists of air bubbles of magnitude with an average of about 130 micrometers (40-250 micrometers of ranges) separately prepared with the resin system frothing agent which added methyl cellulose 0.1% was added to the above-mentioned slurry, and it agitated by the propeller type mixer. It was 0.81, when this bubble slurry was cast to the casting rate plaster mold for /of 80 micrometers, it unmolded 22 hours after and the bulk specific gravity of the acquired Plastic solid was measured. Moreover, observation of the fracture surface of this Plastic solid checked that a 40-micrometer substantia-compacta layer was introduced into a surface, and 40-1980-micrometer pore was introduced into that interior. Moreover, pore was a globular form mostly and was the structure of the hybrid model of independent pore and continuation pore.

[0049] After heating the above-mentioned Plastic solid at 500 degrees C among air for 10 hours and degreasing, the lightweight ceramic Plastic solid of this invention was acquired by performing baking at 1400 degrees C for 2 hours. At this time, when a big camber or a big crack

were not accepted in a Plastic solid and the fracture surface of a Plastic solid was observed, it was checked that a 35-micrometer substantia-compacta layer is introduced into a surface, and 32-1800-micrometer pore is introduced into that interior. Moreover, the result investigated about the porosity from the surface of a Plastic solid to a core is shown in drawing 2 . This shows that porosity is increasing from the surface portion continuously toward a core. [0050] Furthermore, measurement about the porosity of the acquired Plastic solid, reinforcement, a spalling-proof property, etc. was also performed. The result is shown in a table 4. [0051] After casting using example of comparison 4 casting rate the plaster mold for /of 120 micrometers, it unmolded 15 hours after, and also the Plastic solid was produced like the example 4. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 4 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 4. [0052] [A table 4]

[0053] It turns out that especially this invention Plastic solid that porosity increases from the result of a table 4 in dip demonstrates the effect excellent in thermal shock resistance. [0054] an average of [which was separately prepared with the resin system frothing agent which added example 5 methyl cellulose 0.1%] -- 250ml of foam liquid which consists of air bubbles with a magnitude of about 70 micrometers (30-200 micrometers of ranges) was added, and the Plastic solid was produced like the example 4 except having carried out 30 hours after, since stripping was cast. [0055] The investigated result is shown in drawing 2 about the porosity of the above-mentioned Plastic solid, and the porosity of a Plastic solid, reinforcement, a spalling-proof property, etc. are shown in a table 5. [0056] After casting using example of comparison 5 casting rate the plaster mold for /of 120 micrometers, it unmolded 11 hours after, and also the Plastic solid was produced like the example 5. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 5 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 5. [0057] [A table 5]

[0058] an average of [which was separately prepared with the protein system frothing agent which added example 6 methyl cellulose 0.1%] -- 400ml of foam liquid which consists of air bubbles with a magnitude of about 210 micrometers (100-350 micrometers of ranges) was added, and the Plastic solid was produced like the example 4 except having carried out 30 hours after, since stripping was cast.

[0059] The investigated result is shown in drawing 2 about the porosity of the above-mentioned Plastic solid, and the porosity of a Plastic solid, reinforcement, a spalling-proof property, etc. are shown in a table 6.

[0060] After casting using example of comparison 6 casting rate the plaster mold for /of 120 micrometers, it unmolded 23 hours after, and also the Plastic solid was produced like the example 5. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 6 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 6.

[0061]

[A

table

6]

[0062] After having prepared the bubble slurry like example 7 example 1, having impressed the plate electrode made from stainless steel to this by initial-voltage 200V, lowering to 100V gradually in 2 hours and performing electrophoresis cast, unmolding, desiccation, degreasing, and baking were performed like the example 1. Change of the porosity from a surface to a core is shown in drawing 1 . This shows that porosity is increasing from the surface portion continuously toward a core.

[0063] Furthermore, measurement about the porosity of the acquired Plastic solid, reinforcement, a spalling-proof property, etc. was also performed. The result is shown in a table 7. In addition, the result of an example 1 is also written together for reference.

[0064]

[A

table

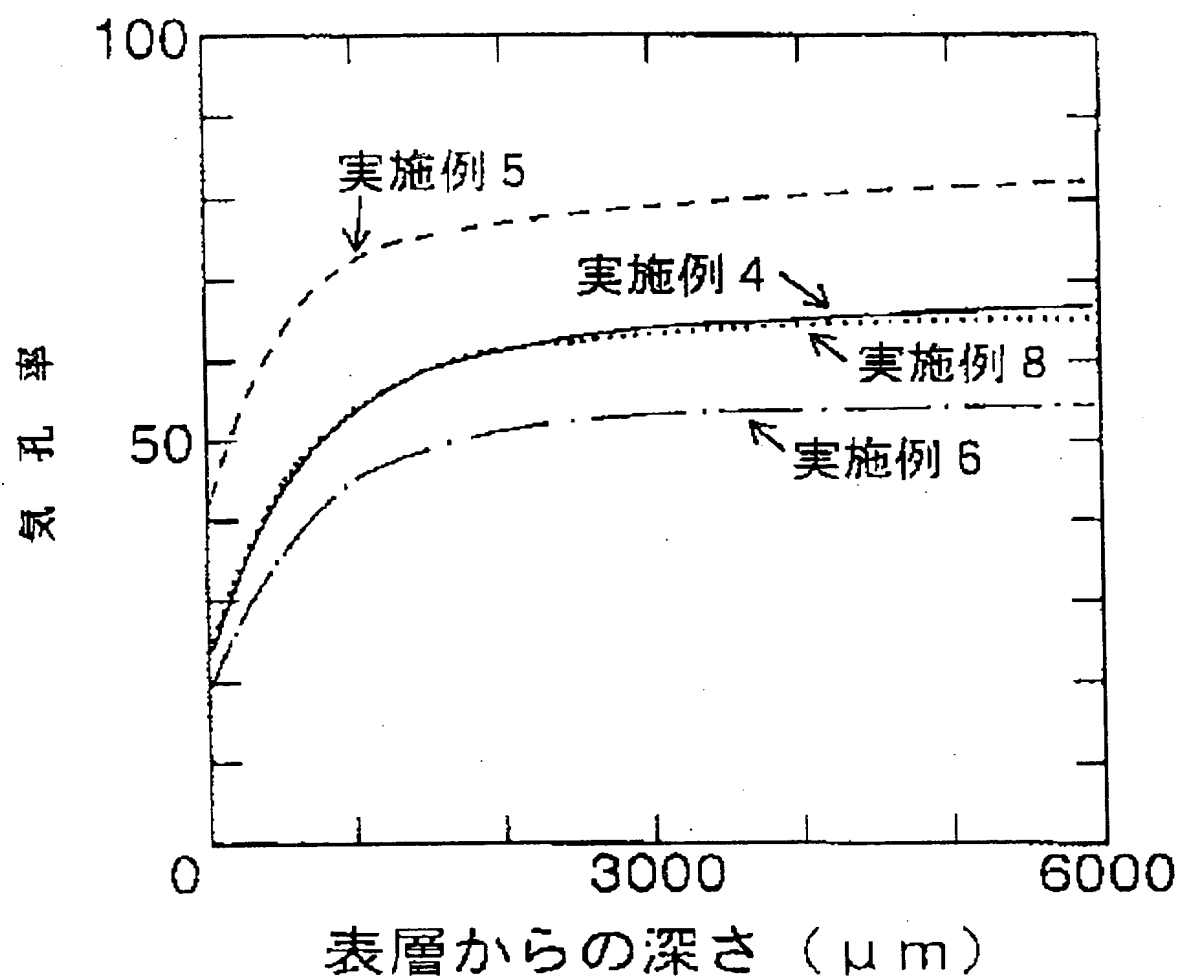
7]

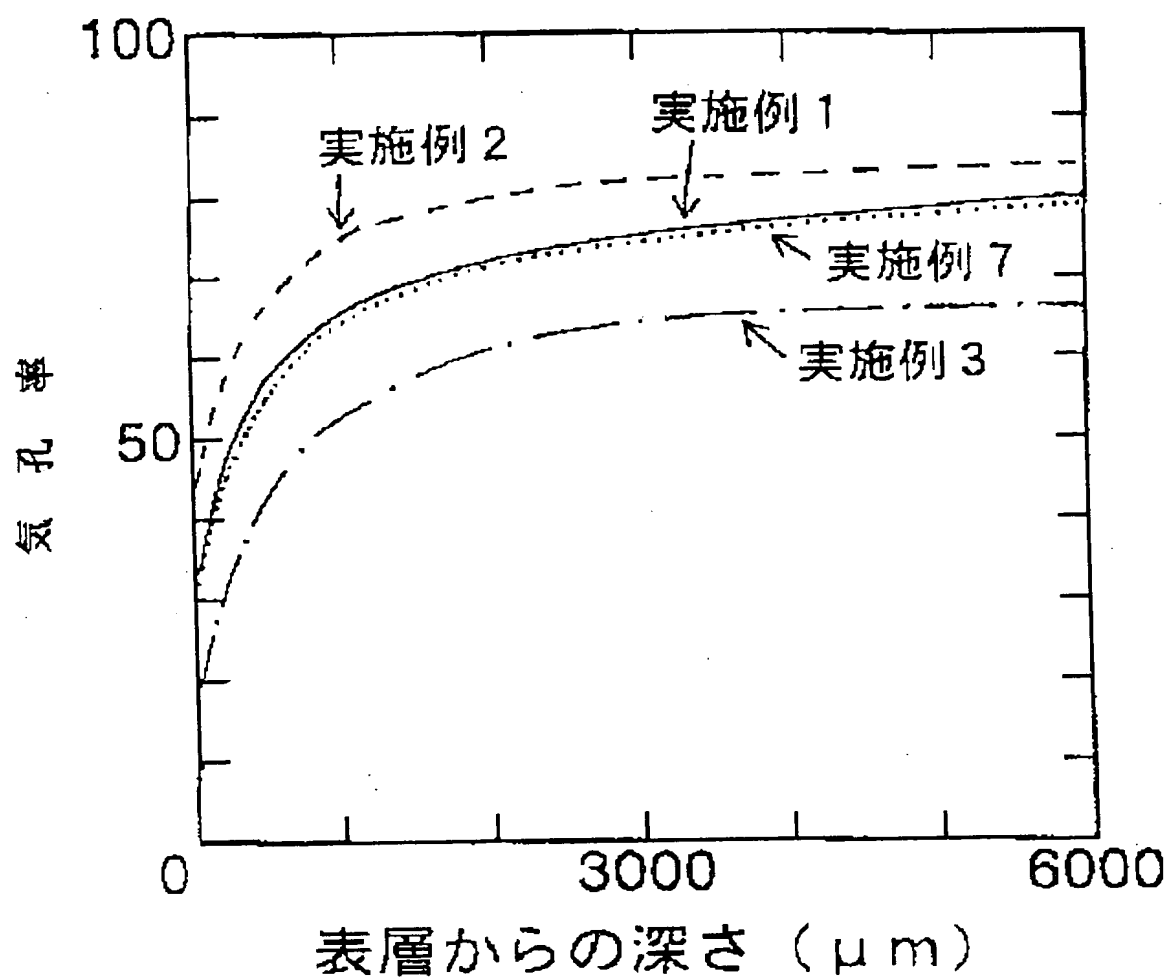
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continuously toward a core.
[0066] Furthermore, measurement about the porosity of the acquired Plastic solid, reinforcement, a spalling-proof property, etc. was also performed. The result is shown in a table 8. In addition, the result of an example 4 is also written together for reference.
[0067]
[A table 8]

[0068] As mentioned above, by having the unique structure where porosity increases this invention Plastic solid from a surface portion continuously toward a core shows that the especially excellent thermal shock resistance can be demonstrated.

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[0013] As for especially porosity of the whole Plastic solid, it is usually desirable that it is 50 - 80% about 30 to 90%. It stops being able to demonstrate a property as a lightweight object and is not desirable when the above-mentioned porosity is less than 30%. If it exceeds 90%, reinforcement will fall. In addition, although magnitude of pore is based also on construction material which constitutes a Plastic solid, it is usually about 20-4000 micrometers.

[0014] A substantia-compacta layer usually exists covering a depth of 5-50 micrometers from a front face of a Plastic solid. A substantia-compacta layer as used in the field of [here] this invention means a layer whose porosity is usually about 0 - 5%. When [both] this substantia-compacta layer is less than 5 micrometers and a film from a front face, surface smooth nature and reinforcement fall. In addition, when high reinforcement is required, in a range which does not spoil lightweight nature, thickness from a front face may exceed 50 micrometers. Moreover, when thickness of a Plastic solid is thick, in a range which does not exceed one fourth of the thickness, you may exceed 50 micrometers.

[0015] In addition, smoothness (Rmax) on a front face of a Plastic solid is usually about 3-50 micrometers that what is necessary is just to set up suitably according to the amount of organic substances contained in a calcinated object, baking speed, and surface precision of a calcinated object. in addition -- since the larger one of surface roughness is advantageous also from a point which promotes degreasing when a precise field is not required -- the above -- you may become out of range and an embossing pattern may be made if needed.

[0016] A Plastic solid of this invention has structure where porosity increases from the above-mentioned substantia-compacta layer continuously toward a Plastic solid core. an increment in porosity -- it changes comparatively (dip of porosity) with manufacture conditions, raw materials to be used, and although it is not uniform, as shown, for example in after-mentioned drawing 1 or after-mentioned drawing 2 , with porosity alumina ceramics, a surface to the fixed depth is comparatively high, and it has become comparatively loose dip after that. As for porosity of a Plastic solid core, it is desirable to consider as a maximum of 95% from a strong point. In this invention Plastic solid with such unique structure, as a result of controlling progress of a crack and being able to prevent growth of a crack since porosity becomes small as it goes to a Plastic solid front face even if a crack occurs inside a Plastic solid, outstanding thermal shock resistance is discovered.

[0017] In addition, since stress concentration as a defect tends to happen the more the more it

becomes a long and slender configuration, pore in a Plastic solid has a desirable thing near a globular form as much as possible. Moreover, you may be the thing of structure of continuation pore, independent pores, or these hybrid models.

[0018] Next, a manufacture method of a Plastic solid of this invention is explained.

[0019] A ceramic slurry is prepared first. Using powder of ceramics of construction material of said Plastic solid as a raw material, water is added and a slurry is prepared according to a conventional method. As for loadings of water, it is desirable to usually consider as 20 - 50 weight section to the ceramic raw material 100 weight section. Adjustment of a slurry becomes difficult at a case of under 20 weight sections. Moreover, if 50 weight sections are exceeded, hardening after casting will take long duration. Moreover, in this invention, various additives, such as well-known lubricant and a dispersant, may be added if needed.

[0020] Next, air bubbles are introduced into a slurry by [which add and agitate foam liquid separately prepared with a foaming agent to the above-mentioned slurry] depending especially, or adding and stirring a direct frothing agent to the above-mentioned slurry.

[0021] What forms air bubbles in a ceramic slurry by adding and mixing is named a frothing agent which foam liquid said to this invention means a foamy object which consists of air bubbles prepared with a well-known foaming agent etc. here, and is said to this invention generically. That is, the above-mentioned frothing agent will not be limited especially if air bubbles can be built, but a foaming agent, a frothing agent, a surfactant, etc. are included by foaming agent of this invention. Specifically as a foaming agent, alkylbenzene sulfonates, a high-class alkylamino acid, etc. can be illustrated as surfactants, such as a protein system frothing agent and an albumen, as frothing agents, such as aluminum impalpable powder and silicon impalpable powder. In addition, it is desirable to use a protein system frothing agent in respect of a low price especially in this invention. Moreover, in this invention, a well-known thickener, a sizing agent, etc. can also be added suitably if needed. As a thickener, a sizing agent, etc., methyl cellulose, polyvinyl alcohol, saccharose, molasses, etc. are illustrated. By adding these, improvement in reinforcement of air bubbles in a slurry can be aimed at, and air bubbles can be stabilized. What is necessary is just to produce preparation of foam liquid with a conventional method using the above-mentioned foaming agent etc.

[0022] A slurry which introduced air bubbles is slushed into molds, such as a plaster mold, and a slip casting is performed according to a conventional method. In this case, although solid content which is floating on a cellular front face moves to a surface, the porosity slope characteristic of a Plastic solid can be given and controlled by casting that passing speed and considering as the following by 80-micrometer/preferably hereafter by 110-micrometer/with a casting rate in early stages of a mold. That is, when a slip casting is performed, air bubbles are first crushed by plaster mold front face, a substantia-compacta layer is formed, after that, a casting rate becomes slow gradually by formation of a substantia-compacta layer, and air bubbles come to remain. After a while, as a result of a casting rate's becoming slow further, and a path of air bubbles which remain inside a Plastic solid becoming large and the amount of air bubbles also increasing, a lightweight ceramic Plastic solid to which porosity changed from a surface toward a core is acquired.

[0023] When the above-mentioned casting rate exceeds a part for 120-micrometer/, it becomes difficult to give the slope characteristic of porosity. That is, since distribution of pore equalizes, it is not desirable. What is necessary is for there to be especially no limit and just to set it up suitably by a use of a Plastic solid etc., as long as a minimum of a casting rate can shut up air bubbles in a Plastic solid.

[0024] Moreover, if a casting rate is generally made quick, there is an inclination for a substantia-compacta layer to become thick. therefore -- for example, a thick substantia-compacta layer is the need -- occasionally -- a casting rate -- about 80-110micrometers/minute -- then, a 10-100-micrometer substantia-compacta layer can be made to usually form Furthermore, it is also possible to adjust water absorption of a plaster mold, putting in a plaster mold into a

decompression device and controlling a pressure, and to control a substantia-compacta layer in desired thickness.

[0025] It is also possible to control a degree of dip of porosity of a Plastic solid by this invention by inserting a positive electrode of a configuration of arbitration and a porous electrode of a negative electrode in a slurry which introduced air bubbles, and impressing voltage. That is, although solid content which is floating on a cellular front face moves with air bubbles toward an electrode of particle electrification and objection by impression of voltage, by changing voltage in this case, passing speed of the above-mentioned solid content can be controlled, and a dip degree can be changed. What is necessary is just to usually let voltage which should be impressed be the direct current voltage of 100-200V. Since a substantia-compacta layer will become is hard to be formed as a result of passing speed's becoming quick too much if migration of solid content is not enough and exceeds 200V, it is not desirable less than [100V]. Although it changes with a use of a Plastic solid, and classes of construction material, a control method of voltage can be performed by lowering voltage gradually, after it makes a substantia-compacta layer form and a substantia-compacta layer becomes desired thickness by impressing voltage of 200V first, for example.

[0026] Subsequently, if a conventional method is followed, it unmolds and degreases and it subsequently calcinates, this invention Plastic solid will be acquired. What is necessary is just to usually perform baking conditions at about 1300-1700 degrees C for about 1 to 5 hours.

[0027]

[Effect of the Invention] By the manufacture method of this invention, the ceramic Plastic solid which has the unique structure where porosity increases continuously especially the ceramic slurry that introduced air bubbles into the large quantity toward a Plastic solid core from the above-mentioned substantia-compacta layer since it fabricates by the slip casting, controlling a casting rate can be acquired.

[0028] It can demonstrate the outstanding thermal shock resistance while it has high reinforcement and surface smooth nature, although this invention Plastic solid is porosity. It is broadly utilizable for the use of the sagger for baking, a setter, a shelf board, heat insulating brick, etc. using the unique structure.

[0029]

[Example] An example and the example of a comparison are shown below, and the place by which it is characterized [of this invention] is made still clearer.

[0030] The lightweight ceramic Plastic solid was produced using alumina system ceramic powder as example 1 raw material.

[0031] First, 100g of water, 1.5g of polyacrylic acid ammonium salt system dispersants, and 1.5g of paraffin series wax system lubricant were added to 300g of alumina system ceramic powder, and the ceramic slurry was prepared by agitating by the propeller type mixer.

[0032] Subsequently, 300ml of foam liquid which consists of air bubbles of magnitude with an average of about 150 micrometers (20-230 micrometers of ranges) separately prepared with the protein system frothing agent which added saccharose 0.2% was added to the above-mentioned slurry, and it was agitated by the propeller type mixer. It was 0.62, when this bubble slurry was cast to the casting rate plaster mold for /of 80 micrometers, it unmolded 24 hours after and the bulk specific gravity of the acquired generation form was measured. Moreover, observation of the fracture surface of this Plastic solid checked that a 35-micrometer substantia-compacta layer was introduced into a surface, and 40-1500-micrometer pore was introduced into that interior. Moreover, pore was a globular form mostly and was the structure of the hybrid model of independent pore and continuation pore.

[0033] After heating the above-mentioned Plastic solid at 600 degrees C among air for 5 hours and degreasing, the lightweight ceramic Plastic solid of this invention was acquired by performing baking at 1500 degrees C for 2 hours. At this time, when a big camber or a big crack were not accepted in a Plastic solid and the fracture surface of a Plastic solid was observed, it

was checked that a 30-micrometer substantia-compacta layer is introduced into a surface, and 30-1200-micrometer pore is introduced into that interior. Moreover, the result investigated about the porosity from the surface of a Plastic solid to a core is shown in drawing 1 . This shows that porosity is increasing from the surface portion continuously toward a core. [0034] Furthermore, measurement about the porosity of the acquired Plastic solid, reinforcement, a spalling-proof property, etc. was also performed. The result is shown in a table 1. [0035] After casting using example of comparison 1 casting rate the plaster mold for /of 120 micrometers, it unmolded 16 hours after, and also the Plastic solid was produced like the example 1. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 1 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 1. [0036] [A table 1]

[0037] It turns out that especially this invention Plastic solid that porosity increases from the result of a table 1 in dip demonstrates the effect excellent in thermal shock resistance. [0038] an average of [which was separately prepared with the protein system frothing agent which added example 2 saccharose 0.2%] -- 200ml of foam liquid which consists of air bubbles with a magnitude of about 50 micrometers (10-120 micrometers of ranges) was added, and the Plastic solid was produced like the example 1 except having carried out 20 hours after, since stripping was cast. [0039] The investigated result is shown in drawing 1 about the porosity of the above-mentioned Plastic solid, and the porosity of a Plastic solid, reinforcement, a spalling-proof property, etc. are shown in a table 2. [0040] After casting using example of comparison 2 casting rate the plaster mold for /of 120 micrometers, it unmolded 12 hours after, and also the Plastic solid was produced like the example 1. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 2 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 2. [0041] [A table 2]

[0042] an average of [which was separately prepared with the protein system frothing agent which added example 3 saccharose 0.2%] -- 400ml of foam liquid which consists of air bubbles with a magnitude of about 200 micrometers (100-300 micrometers of ranges) was added, and the Plastic solid was produced like the example 1 except having carried out 32 hours after, since stripping was cast.

[0043] The investigated result is shown in drawing 1 about the porosity of the above-mentioned Plastic solid, and the porosity of a Plastic solid, reinforcement, a spalling-proof property, etc. are shown in a table 3.

[0044] After casting using example of comparison 3 casting rate the plaster mold for /of 120 micrometers, it unmolded 25 hours after, and also the Plastic solid was produced like the example 3. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 3 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 3.

[0045]

[A table 3]

[0046] The lightweight ceramic Plastic solid was produced using silicon nitride system ceramic powder as example 4 raw material.

[0047] First, 100g of water, 3.5g of polyacrylic acid ammonium salt system dispersants, and 1.5g of paraffin series wax system lubricant were added to 300g of silicon nitride system ceramic powder, and the ceramic slurry was prepared by agitating by the propeller type mixer.

[0048] Subsequently, 300ml of foam liquid which consists of air bubbles of magnitude with an average of about 130 micrometers (40-250 micrometers of ranges) separately prepared with the resin system frothing agent which added methyl cellulose 0.1% was added to the above-mentioned slurry, and it agitated by the propeller type mixer. It was 0.81, when this bubble slurry was cast to the casting rate plaster mold for /of 80 micrometers, it unmolded 22 hours after and the bulk specific gravity of the acquired Plastic solid was measured. Moreover, observation of the fracture surface of this Plastic solid checked that a 40-micrometer substantia-compacta layer was introduced into a surface, and 40-1980-micrometer pore was introduced into that interior. Moreover, pore was a globular form mostly and was the structure of the hybrid model of independent pore and continuation pore.

[0049] After heating the above-mentioned Plastic solid at 500 degrees C among air for 10 hours and degreasing, the lightweight ceramic Plastic solid of this invention was acquired by performing baking at 1400 degrees C for 2 hours. At this time, when a big camber or a big crack

were not accepted in a Plastic solid and the fracture surface of a Plastic solid was observed, it was checked that a 35-micrometer substantia-compacta layer is introduced into a surface, and 32-1800-micrometer pore is introduced into that interior. Moreover, the result investigated about the porosity from the surface of a Plastic solid to a core is shown in drawing 2 . This shows that porosity is increasing from the surface portion continuously toward a core. [0050] Furthermore, measurement about the porosity of the acquired Plastic solid, reinforcement, a spalling-proof property, etc. was also performed. The result is shown in a table 4. [0051] After casting using example of comparison 4 casting rate the plaster mold for /of 120 micrometers, it unmolded 15 hours after, and also the Plastic solid was produced like the example 4. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 4 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 4. [0052] [A table 4]

[0053] It turns out that especially this invention Plastic solid that porosity increases from the result of a table 4 in dip demonstrates the effect excellent in thermal shock resistance. [0054] an average of [which was separately prepared with the resin system frothing agent which added example 5 methyl cellulose 0.1%] -- 250ml of foam liquid which consists of air bubbles with a magnitude of about 70 micrometers (30-200 micrometers of ranges) was added, and the Plastic solid was produced like the example 4 except having carried out 30 hours after, since stripping was cast. [0055] The investigated result is shown in drawing 2 about the porosity of the above-mentioned Plastic solid, and the porosity of a Plastic solid, reinforcement, a spalling-proof property, etc. are shown in a table 5. [0056] After casting using example of comparison 5 casting rate the plaster mold for /of 120 micrometers, it unmolded 11 hours after, and also the Plastic solid was produced like the example 5. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 5 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 5. [0057] [A table 5]

[0058] an average of [which was separately prepared with the protein system frothing agent which added example 6 methyl cellulose 0.1%] -- 400ml of foam liquid which consists of air bubbles with a magnitude of about 210 micrometers (100-350 micrometers of ranges) was added, and the Plastic solid was produced like the example 4 except having carried out 30 hours after, since stripping was cast.

[0059] The investigated result is shown in drawing 2 about the porosity of the above-mentioned Plastic solid, and the porosity of a Plastic solid, reinforcement, a spalling-proof property, etc. are shown in a table 6.

[0060] After casting using example of comparison 6 casting rate the plaster mold for /of 120 micrometers, it unmolded 23 hours after, and also the Plastic solid was produced like the example 5. Internal porosity was uniform, although the thickness of relative bulk density and a substantia-compacta layer and the whole porosity were the same as that of the Plastic solid of an example 6 almost when the acquired Plastic solid was investigated. The result of having also performed measurement about the reinforcement of the acquired Plastic solid, a spalling-proof property, etc. is shown in a table 6.

[0061]

[A

table

6]

[0062] After having prepared the bubble slurry like example 7 example 1, having impressed the plate electrode made from stainless steel to this by initial-voltage 200V, lowering to 100V gradually in 2 hours and performing electrophoresis cast, unmolding, desiccation, degreasing, and baking were performed like the example 1. Change of the porosity from a surface to a core is shown in drawing 1 . This shows that porosity is increasing from the surface portion continuously toward a core.

[0063] Furthermore, measurement about the porosity of the acquired Plastic solid, reinforcement, a spalling-proof property, etc. was also performed. The result is shown in a table 7. In addition, the result of an example 1 is also written together for reference.

[0064]

[A

table

7]

[0065] After having prepared the bubble slurry like example 8 example 4, having impressed the plate electrode made from stainless steel to this by initial-voltage 200V, lowering to 100V gradually in 2 hours and performing electrophoresis cast, unmolding, desiccation, degreasing, and baking were performed like the example 4. Change of the porosity from a surface to a core is shown in drawing 2 . This shows that porosity is increasing from the surface portion

continuously toward a core.
[0066] Furthermore, measurement about the porosity of the acquired Plastic solid, reinforcement, a spalling-proof property, etc. was also performed. The result is shown in a table 8. In addition, the result of an example 4 is also written together for reference.
[0067]
[A table 8]

[0068] As mentioned above, by having the unique structure where porosity increases this invention Plastic solid from a surface portion continuously toward a core shows that the especially excellent thermal shock resistance can be demonstrated.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] It is the Plastic solid which consists of an oxide system or non-oxide system ceramics, and is (a). Porosity of the whole Plastic solid is 30 - 90%, and it is (b). A substantia-compacta layer exists covering a depth of 5-50 micrometers from a front face, and it is (c). A porosity dip mold lightweight ceramic Plastic solid characterized by porosity increasing from the substantia-compacta layer concerned continuously toward a Plastic solid core.

[Claim 2] A manufacture method of a porosity dip mold lightweight ceramic Plastic solid characterized by unloading, degreasing and calcinating after a diameter of air bubbles carries out the slip casting of the slurry which adds and comes to agitate foam liquid which is 10-2000 micrometers to an oxide system or a non-oxide system ceramic powder slurry below by casting rate/of 110 micrometers.

[Claim 3] A manufacture method according to claim 2 in which a casting rate carries out a slip casting below by 80-micrometer/.

[Claim 4] A manufacture method according to claim 2 or 3 characterized by controlling a dip degree of porosity of a Plastic solid acquired by carrying out a slip casting, impressing voltage to a slurry.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief	Description	of	the	Drawings]
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[Drawing 1] It is the drawing in which change of the porosity from the surface of this invention Plastic solid in examples 1-3 and an example 7 to a core is shown.

[Drawing 2] It is the drawing in which change of the porosity from the surface of this invention Plastic solid in examples 4-6 and an example 8 to a core is shown.

[Translation done.]